

# Supporting Information

## Remarkably Stable Fischer-type $\alpha$ -Carbonyl Copper(I) Carbene Complex: Synthesis, Structure and Activity in Stoichiometric Cyclopropanation of Alkenes

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## Experimental section

Unless otherwise stated, all experiments were performed under an Ar atmosphere using a Braun glove box or by Schlenk technique. Tetrahydrofuran, pentane, hexane, toluene and diethyl ether were distilled over benzophenone sodium-ketyl and kept under Ar. Toluene- $d_8$  was stirred over  $CaH_2$  and then degassed trice prior to use. Tetrahydrofuran- $d_8$  was distilled over sodium and degassed trice. Pyridine, piperidine,  $iPr_2NH$  and  $NEt_3$  were distilled under Ar over KOH. DBU was purified by vacuum distillation. Commercially available EDA was distilled in vacuum prior to use and filled with Ar. Styrene and p-methylstyrene were distilled in vacuum prior to use and degassed trice. p-Methoxystyrene and p-(trifluoromethyl)styrene were passed through a short neutral  $Al_2O_3$  column and degassed trice. All the other commercially available reagents were used as received. The solutions of LDA [lithium diisopropylamide] were freshly prepared from  $iPr_2NH$  and  $nBuLi$  and used immediately. Ethyl diazo(4-nitrophenyl)acetate,<sup>[1]</sup>  $TsN_3$  [tosylazide],<sup>[2]</sup>  $TryN_3$  [2,4,6-tri(isopropyl)benzenesulphonyl azide],<sup>[3]</sup> and complex **1**,<sup>[4]</sup> were prepared according to known procedures.

The NMR spectra were recorded on Bruker 500, 300 or 250 MHz spectrometers at temperatures specified below.  $^1H$ ,  $^{13}C$  NMR chemical shifts are reported in parts per million and are referenced to the deuterated solvent used.  $^{31}P$  NMR spectra are calibrated either with external 85%  $H_3PO_4$  or, where possible, by traces of free iminophosphanamide ligand ( $\delta$  30.1). All the  $^{13}C$  and  $^{31}P$  NMR spectra were broad-band decoupled on  $^1H$ . Mass-spectra were recorded on a JMS 700 (JOEL). Elemental analyses were performed in the "Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg".

The solutions of copper carbenes **6** and **8g** and olefins for kinetic measurements were prepared using a volumetric flask, divided in equivalent portions and kept at -78 °C. All kinetic studies were performed by the  $^1H$  NMR spectroscopy using Bruker 500 MHz NMR spectrometer equipped with an internal thermocouple sensor. The sample was allowed to reach thermo-equilibrium for ca. 4 min prior to measurements. The  $\sigma$  and  $\sigma^+$  values, the errors of the rate constants and the activation parameters were calculated as described in [5].

Ethyl diazo(2-nitrophenyl)acetate<sup>[6]</sup>. To a well-stirred solution ethyl (2-nitrophenyl)acetate (300 mg, 1.434 mmol), Bu<sub>4</sub>NBr (0.28 eq., 130 mg, 0.403 mmol), 18-crown-6 (13 mg), TsN<sub>3</sub> (230 mg) in 15 ml of C<sub>6</sub>H<sub>6</sub> was added dropwise a 20% aqueous solution of KOH (15 ml). Reaction mixture was stirred at 38 °C 1 h, and the benzene phase slowly acquired a yellow color. The temperature was maintained at 40 °C for 1.5 h, and the organic layer changed its color to red. TLC-control showed almost complete conversion of the starting material. Additional 40 mg of TsN<sub>3</sub> were added, and stirring was continued at 38 °C for 40 min. Et<sub>2</sub>O was added, and the organic phase was separated. Water phase was diluted with H<sub>2</sub>O (20 ml) and extracted with Et<sub>2</sub>O (15 ml). Combined organic extracts were washed with H<sub>2</sub>O (20 ml), brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give a yellow oil which was purified by column chromatography (100 ml SiO<sub>2</sub>, EtOAc/hexane 1:5) to yield 0.26 g (77%) of a yellow-orange oil. Crystallization from EtOH gave an analytical sample. M. p. 48 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.82-7.85 (m, 1H arom.); 7.42-7.49 (m, 1H arom.); 7.24-7.36 (m, 2H arom.); 4.08 (q, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, OCH<sub>2</sub>); 1.09 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3</sub>).

*tert*-Butyl (4-nitrophenyl)acetate<sup>[7]</sup>. A 100-ml flask equipped with a calcium chloride drying tube and a magnetic stirring bar was charged with (4-nitrophenyl)acetic acid (5 g, 27.6 mmol), dry CH<sub>2</sub>Cl<sub>2</sub> (50 ml), *t*BuOH (8 ml, 82.20 mmol) and (DMAP) (2.70 g, 22.08 mmol). The solution was stirred and cooled in an ice bath to 0 °C while carboxydiimide (8.20 g, 39.75 mmol) was added in three portions. The reaction mixture was stirred at 0 °C for 15 min, then the cool bath was removed and stirring was continued at r. t. for 34 hours. During this time, a white precipitate was formed. The reaction mixture was filtered through a celite. The celite was washed with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic fractions were washed with cold concentrated citric acid (2×30 ml), cold saturated NaHCO<sub>3</sub> (2×30 ml), brine (30 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The product was purified by column chromatography (SiO<sub>2</sub>, EtOAc-hexane 1:7) to yield 6.05 g (75%) of colorless liquid, which crystallized on storage in the fridge. Analytical sample was obtained by recrystallization of the product from hexane. Yield 4.24 g (65%). M.p. 55 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  8.17 (d, <sup>3</sup>J<sub>HH</sub> = 8.75 Hz, 2H arom.); 7.43 (d, <sup>3</sup>J<sub>HH</sub> = 8.75 Hz, 2H arom.); 3.63 (s, 2H, ArCH<sub>2</sub>); 1.43 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calc. for C<sub>12</sub>H<sub>15</sub>NO<sub>4</sub> (%): C 60.75, H 6.37, N 5.90. Found: C 60.72, H 6.38, N 5.90.

*tert*-Butyl diazo(4-nitrophenyl)acetate (**7b**). To a mixture of *tert*-butyl (4-nitrophenyl)acetate (1.5 g, 6.325 mmol) and AzN<sub>3</sub> (1.5 eq, 2.28 g, 9.488 mmol) in dry THF (10 ml) was added

Et<sub>3</sub>N (1.5 eq, 1.32 ml, 9.488 mmol). The reaction mixture color became yellow-brown. After 10 min of stirring at room temperature TLC showed the reaction to be not completed. DBU (1.5 eq, 1.42 ml, 9.488 mmol) was added slowly (exothermic reaction) and the reaction mixture was stirred at r. t. for another 10 min, until TLC showed the reaction to be complete. H<sub>2</sub>O was added, and the product was extracted two times with Et<sub>2</sub>O. Combined ether fractions were washed with conc. citric acid (2×30 ml) solution, water (2×30 ml), brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and evaporated on rotary to give a yellow oil. Column chromatography (EtOAc-hexane 1:7) afforded a yellow solid (1.62 g, 97.6 %) which can be recrystallized from EtOAc-hexane 1:7 with addition of small portions of CHCl<sub>3</sub>. Yield after recrystallization 1.46 g (88%), light-yellow solids, m.p. 118-119 °C. The experiment carried out with TsN<sub>3</sub>-piperidine diazo-transfer system gave **7b** in a lower yield (42%). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  8.19 (d, <sup>3</sup>J<sub>HH</sub> = 8.95 Hz, 2H arom.); 7.63 (d, <sup>3</sup>J<sub>HH</sub> = 8.95 Hz, 2H arom.); 1.55 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  162.9 (C=O); 144.8; 134.6; 124.2; 123.1; (all arom. H); 83.2 (C(CH<sub>3</sub>)<sub>3</sub>); 28.3 (C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calc. for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> (%): C 54.75, H 4.98, N 15.96. Found: C 54.72, H 4.91, N 16.00.

*N,N*-diisopropyl-2-(4-nitrophenyl)acetamide. From iPr<sub>2</sub>NH and (4-nitrophenyl)acetic acid chloride followed by purification of the product by column chromatography (EtOAc-petrol ether 1:2.5) and recrystallization from EtOAc-hexane 1:5. The crude product (m. p. 70-71 °C) was used further without additional purification. <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  8.14 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H arom.), 7.39 (d, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, 2H arom.), 3.91 (sep, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1H, NCH(CH<sub>3</sub>)<sub>2</sub>), 3.75 (s, 2H, CH<sub>2</sub>), 3.43 (br. s, 1H, NCH(CH<sub>3</sub>)<sub>3</sub>), 1.37 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 6H, NCH(CH<sub>3</sub>)<sub>3</sub>), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 6H, NCH(CH<sub>3</sub>)<sub>3</sub>).

2-diazo-*N,N*-diisopropyl-2-(4-nitrophenyl)acetamide (**7d**). To a stirred solution of *N,N*-diisopropyl-2-(4-nitrophenyl)acetamide (0.5 g, 1.89 mmol) and AzN<sub>3</sub> (0.5 g, 2.083 mmol) in absolute THF (8 ml) was added dropwise DBU (0.31 ml, 2.083 mmol) at 0 °C. The cool bath was removed and the reaction mixture was stirred at r. t. for ca. 1.5 h (TLC-control). Additional 80 mg of AzN<sub>3</sub> and 0.07 ml of DBU were added, and the dark solution was stirred for further 30 min. The solvent was removed on rotary, and the residue was purified by column chromatography on deactivated SiO<sub>2</sub> (EtOAc-hexane 1:2.5) to give an orange oil which quickly crystallized on standing. The product was recrystallized from warm EtOAc-hexane 1:5. The mother liquor after crystallization was regenerated by evaporation followed by crystallization from light petroleum. Yield 50%, R<sub>f</sub> = 0.95 (EtOAc-hexane = 1:2.5), m. p. 87-88 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  8.18 (d, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, 2H

arom.), 7.28 (d,  $^3J_{\text{HH}} = 9.2$  Hz, 2H arom.), 3.74 (sep,  $^3J_{\text{HH}} = 6.7$  Hz, 2H,  $\text{NCH}(\text{CH}_3)_2$ ), 1.35 (d,  $^3J_{\text{HH}} = 6.7$  Hz, 12H,  $\text{NCH}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$  (%): C 57.92, H 6.25, N 19.30. Found: C 57.77, H 6.20, N 19.18.

*N,N*-dimethyl-2-(4-nitrophenyl)acetamide. (4-nitrophenyl)acetic acid chloride (3 g, 15.04 mmol) was dissolved in dry  $\text{C}_6\text{H}_6$  (100 ml) and the solution was cooled to 0 °C.  $\text{Me}_2\text{NH}$  gas was bubbled through the solution, and a precipitate was formed. The reaction mixture was poured on water, the organic layer was separated, washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give a solid, which was recrystallized from EtOAc-hexane = 1:5 with addition of some EtOAc. Yield 2.58 g (82.4 %), m. p. 89-90 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  8.15 (d,  $^3J_{\text{HH}} = 8.8$  Hz, 2H arom.), 7.40 (d,  $^3J_{\text{HH}} = 8.8$  Hz, 2H arom.), 3.78 (s, 2H,  $\text{CH}_2$ ), 3.03 (s, 3H,  $\text{NCH}_3$ ), 2.96 (s, 3H,  $\text{NCH}_3$ ). Anal. Calc. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$  (%): C 57.69, H 5.81, N 13.45. Found: C 57.59, H 5.78, N 13.40.

2-diazo-*N,N*-dimethyl-2-(4-nitrophenyl)acetamide (**7c**). To a stirred solution of *N,N*-dimethyl-2-(4-nitrophenyl)acetamide (1.2 g, 5.77 mmol) and  $\text{AzN}_3$  (1.52 g, 6.34 mmol) in THF (10 ml) was added DBU (0.95 ml, 6.34 mmol) at 0 °C. The reaction mixture was stirred at r. t. for 1 h, but TLC showed that the reaction had not been completed. Additional  $\text{AzN}_3$  (0.2 g) and DBU (0.2 ml) were added, and the mixture was stirred further for 1 h and then poured on water. The green solution was quenched with ether and shaken. The organic phase was separated and washed with water until no more green (5-6 times). The orange ethereal layer was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The residue was purified by column chromatography on  $\text{SiO}_2$  (EtOAc-hexane 2:1) to give a yellow-orange product. Crystallization from EtOAc-hexane 1:5 (with addition of some EtOAc) gave red-orange plates. Yield 0.61 g (45%), m. p. 118-119 °C.  $^1\text{H}$  NMR (500 MHz, toluene- $d_8$ , 298 K):  $\delta$  7.91 (d,  $^3J_{\text{HH}} = 8.9$  Hz, 2H arom.), 6.98 (d,  $^3J_{\text{HH}} = 8.9$  Hz, 2H arom.), 2.48 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (125.77 MHz, toluene- $d_8$ , 298 K):  $\delta$  162.9 (s,  $\text{C}=\text{O}$ ), 145.2, 135.7, 124.2, 123.4 (all s, arom. C), 62.6 (s,  $\text{C}=\text{N}_2$ ), 36.8 (s,  $\text{N}(\text{CH}_3)_2$ ). Anal. Calc. for  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_3$  (%): C 51.28, H 4.30, N 23.92. Found: C 51.26, H 4.29, N 23.92.

Methyl diazo(4-methoxyphenyl)acetate (**7e**). Method A. To a stirred solution of LDA (1.1 eq., 2.05 mmol) in dry THF (7 ml) at -75 °C was added dropwise via a syringe methyl (4-methoxyphenyl)acetate (0.3 ml, 0.335 g, 1.86 mmol). The reaction mixture was stirred at -75 °C for 1 h followed by dropwise addition of a solution of  $\text{TsN}_3$  (1.15 eq, 420 mg, 2.14 mmol) in THF (2 ml). The reaction mixture was stirred at -75 °C for 10 min, the cool bath

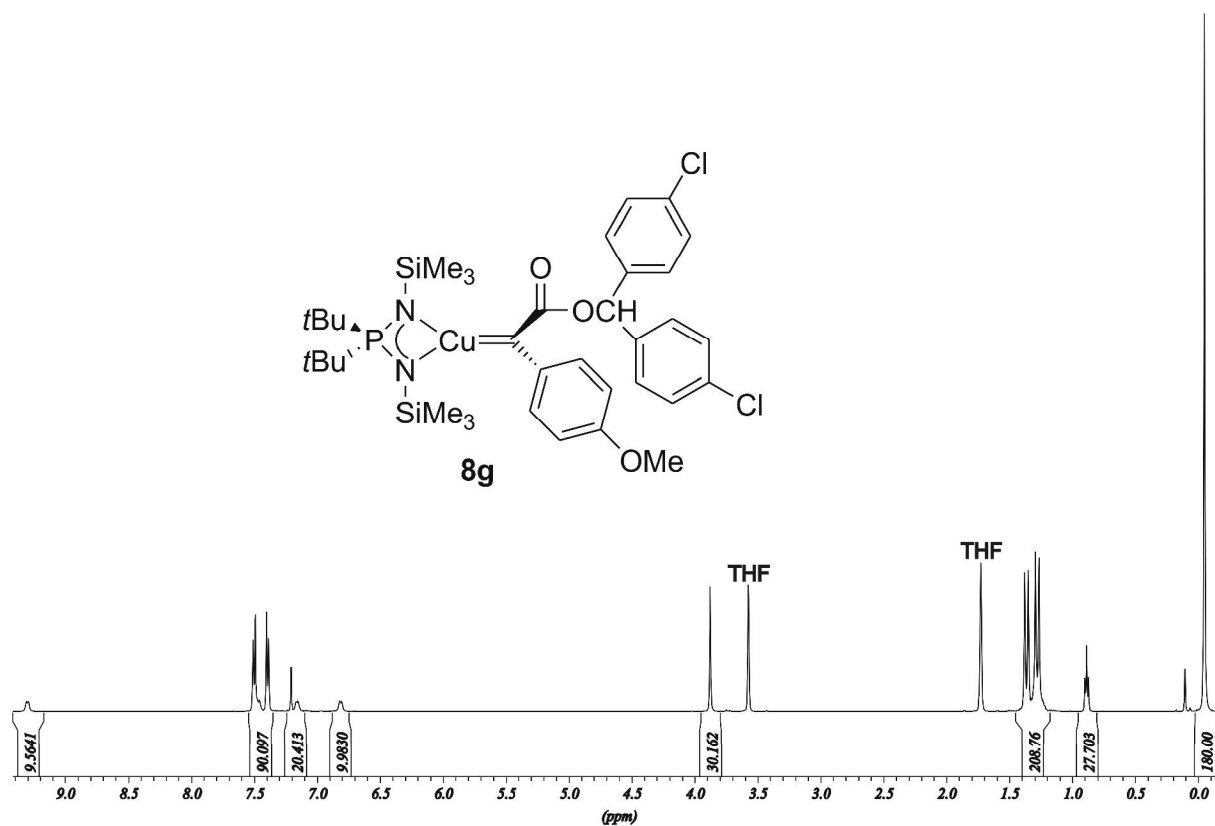
was removed and the mixture was allowed to warm to ambient temperature. Upon warming, a white precipitate was formed, and the viscosity increased. The reaction mixture was stirred at r. t. for 3 h (color change white→orange). After the reaction had been completed (TLC), THF was removed *in vacuo* at <40 °C, the residue was quenched with Et<sub>2</sub>O (40 ml) and H<sub>2</sub>O (30 ml), and the layers separated. The water phase was washed with ether (20 ml), and the combined organic extracts were washed with water (30 ml), brine (20 ml), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated, to give an orange oil which was purified by column chromatography (50 ml SiO<sub>2</sub>, EtOAc-hexane 1:7). Orange solid, 0.34 g (88.7 %). An analytical sample and a sample for carbene synthesis were prepared by crystallization of the product from EtOAc-hexane 1:7 (m. p. 50 °C). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.37 (d, <sup>3</sup>J<sub>HH</sub> = 8.55 Hz, 2H arom.); 6.93 (d, <sup>3</sup>J<sub>HH</sub> = 8.55 Hz, 2H arom.); 3.84 (s, 3H, OCH<sub>3</sub>); 3.80 (s, 3H, OCH<sub>3</sub>). Anal. calc. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub> (%): C 58.25, H 4.89, N 13.59. Found: C 58.17, H 4.84, N 13.63.

Method B.<sup>[6]</sup> To a well-stirred mixture of methyl (4-methoxyphenyl)acetate (0.5 g, 2.78 mmol), Bu<sub>4</sub>NBr (250 mg, 0.778 mmol), TryN<sub>3</sub> (1.2 eq., 1.03 g, 3.336 mmol), 18-crown-6 (30 mg) and C<sub>6</sub>H<sub>6</sub> (10 ml) was added dropwise a 66% aqueous solution of KOH (15 ml). The reaction mixture was stirred at 39 °C for 25 min, and additional 100 mg (0.4 eq.) of trizylazide were added, and the mixture was stirred at 38 °C for another 15 min. Ether was added, and the layers separated. The organic phase was washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. Yield of the product after chromatography (EtOAc-hexane 1:7) 86 mg (15%). Spectroscopic data were identical to a sample prepared by method A.

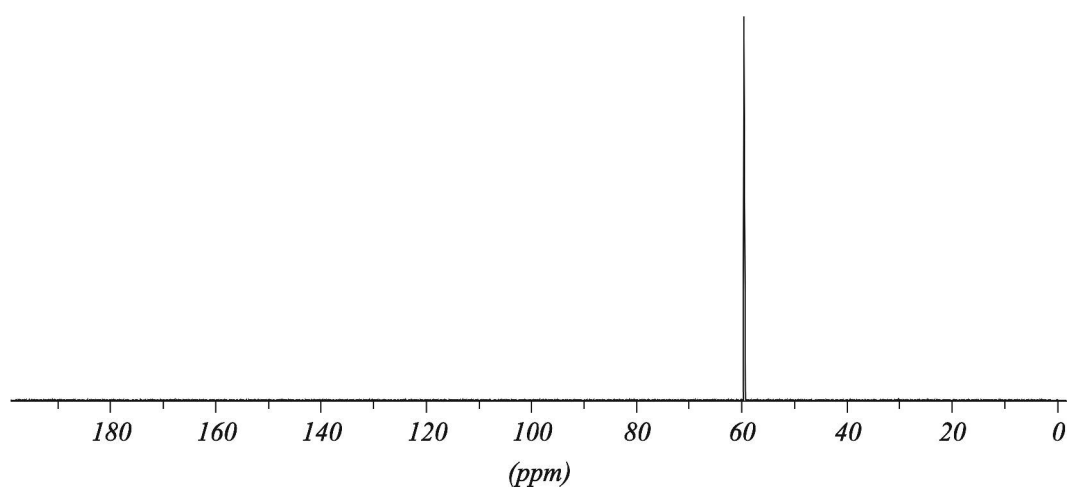
Bis(4-chlorophenyl)methyl (4-methoxyphenyl)acetate. To a solution of bis(4-chlorophenyl)methanol (3.06 g, 12.10 mmol) and pyridine (2.57 ml, 31.85 mmol) in toluene (150 ml) at 0 °C was added dropwise acid chloride (2 ml, 12.74 mmol). The reaction mixture was stirred at r. t. for 2 h, quenched with EtOAc (50 ml) and shaken. The organic phase was separated and washed 3 times with H<sub>2</sub>O and one time with NaHCO<sub>3</sub>, dried and evaporated. The residue was recrystallized from EtOAc-Petrol ether 1:5 and then purified by chromatography (SiO<sub>2</sub>, EtOAc-Petrol ether 1:5). Recrystallization from the same solvent mixture afforded 2.68 g (54.5 %) of analytically pure material, m. p. 95-96 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.31 (d, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz, 4H arom.), 7.21 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H arom.), 7.19 (d, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz, 4H arom.), 6.89 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H arom.), 6.80 (s, 1H, OCH), 3.84 (s, 3H, OCH<sub>3</sub>), 3.69 (s, 2H, ArCH<sub>2</sub>). Anal. calc. for C<sub>22</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>3</sub> (%): C 65.85, H 4.52, Cl 17.67. Found: C 65.64, H 4.54, Cl 17.53.

Bis(4-chlorophenyl)methyl diazo(4-methoxyphenyl)acetate (**7g**). Bis(4-chlorophenyl)methyl (4-methoxyphenyl)acetate (1 g, 2.46 mmol) and  $\text{AzN}_3$  (0.89 g, 3.692 mmol) were suspended in absolute THF, when DBU (0.55 ml, 0.562 g, 3.69 mmol) was added in one portion. The reaction mixture was stirred for 1 h at r. t. and then allowed to stand at ambient temperature in a dark place for 7 days. TLC (EtOAc-hexane 1:7) showed complete conversion of the starting material. The solvent was removed on rotary, and the residue was purified by column chromatography ( $\text{SiO}_2$ , EtOAc-hexane 1:5) to give a red-orange oil that was dried at  $10^{-3}$  mbar. Yield 1.05 g of an orange oil, purity > 90%. The product is light sensitive and slowly decomposes at r. t. so it must be stored under Ar in a dark, cold ( $-35^\circ\text{C}$ ) place.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.27-7.41 (m, 10H arom.), 7.00 (s,  $\text{OCH}_2$ ), 6.97 (d,  $^3J_{\text{HH}} = 8.9$  Hz, 2H arom.), 3.84 (s, 3H,  $\text{OCH}_3$ ). MS-EI: m/z 398.0 (2%)  $[(\text{M}-\text{N}_2)^+]$ .

**Spectra of compound **8g**, its reaction with styrene and  $^{31}\text{P}$  NMR spectra of compounds **8g** and **6** after complete decomposition.**

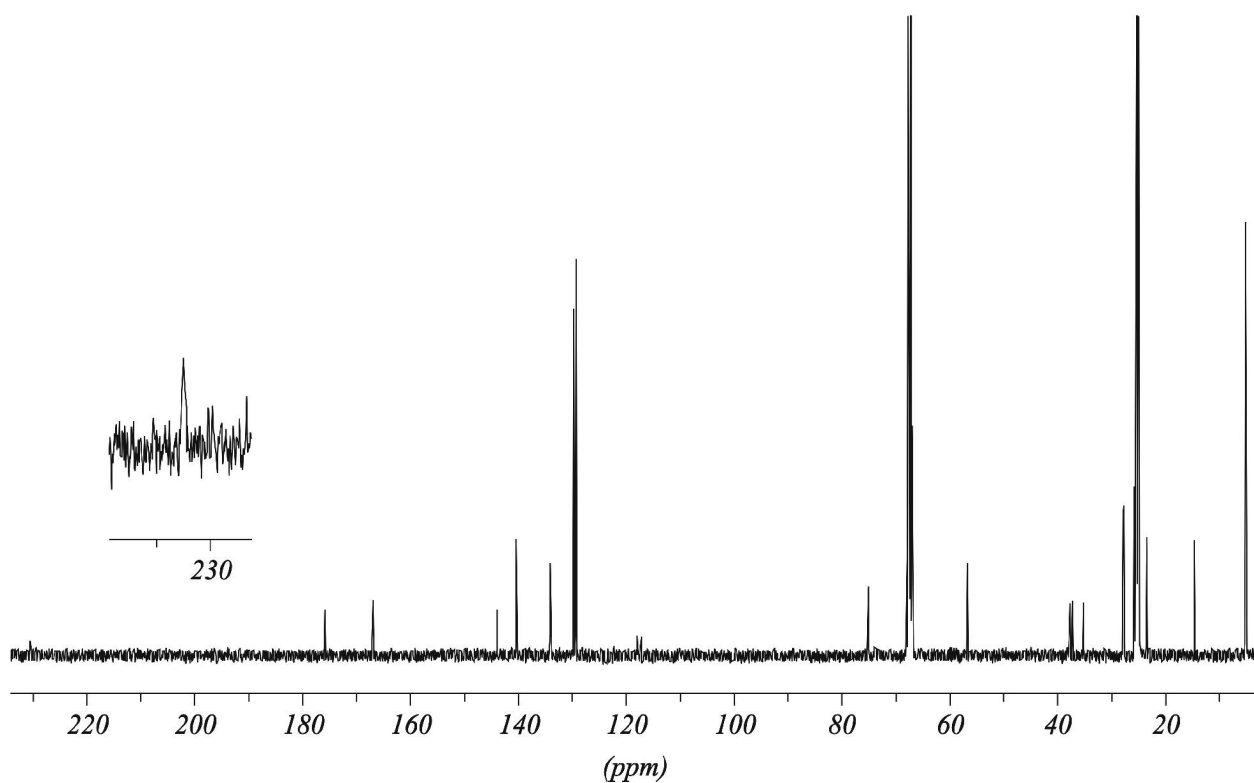


**Figure 1.**  $^1\text{H}$  NMR (500.13 MHz,  $\text{THF-d}_8$ , 238 K) spectrum of the **8g**·0.46  $\text{C}_5\text{H}_{12}$  demonstrating a hindered rotation around the  $\text{C}_{\text{carbene}}\text{-C}_{\text{Ar}}$  bond on NMR time scale at 238K.

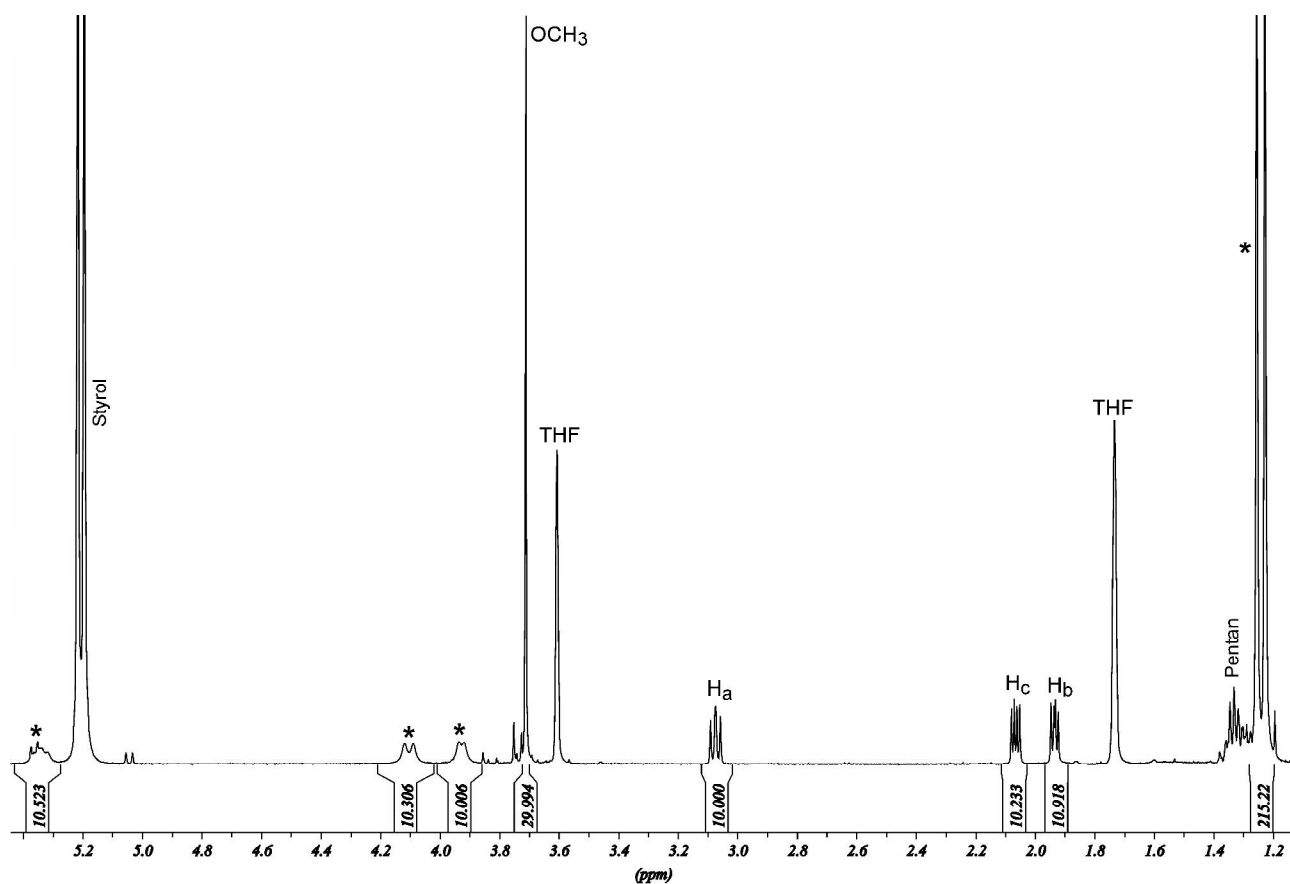


**Figure 2.**  $^{31}\text{P}$  NMR (202.47 MHz,  $\text{THF-d}_8$ , 238 K) spectrum of the **8g**·0.46  $\text{C}_5\text{H}_{12}$ .

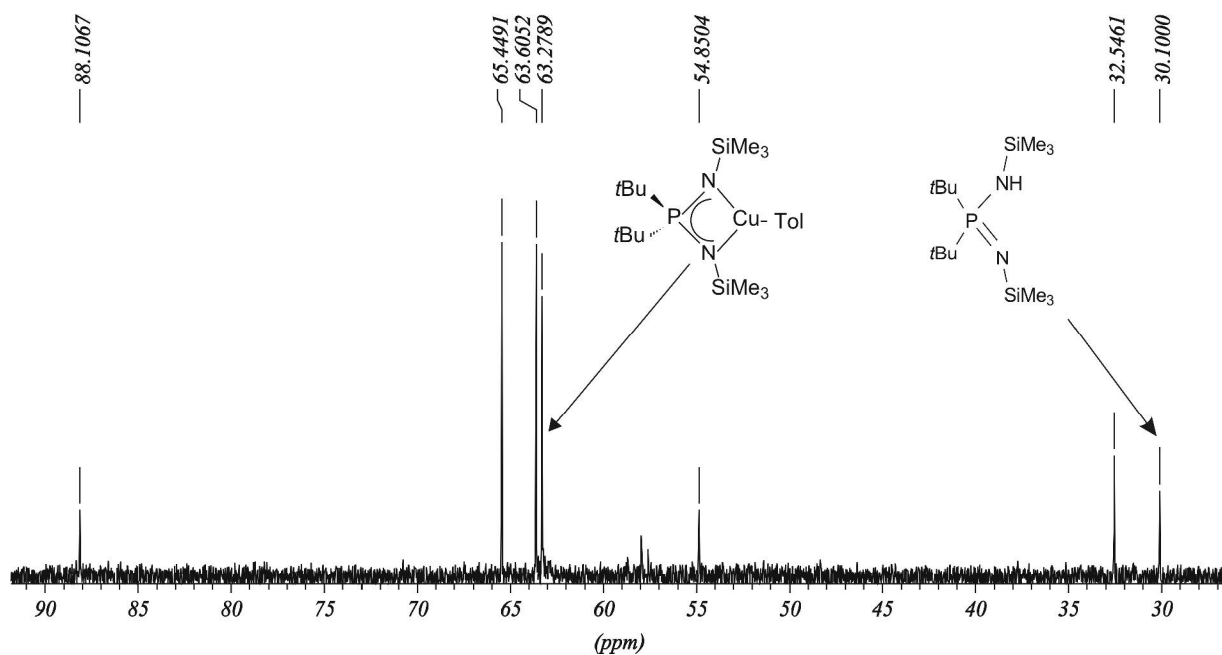




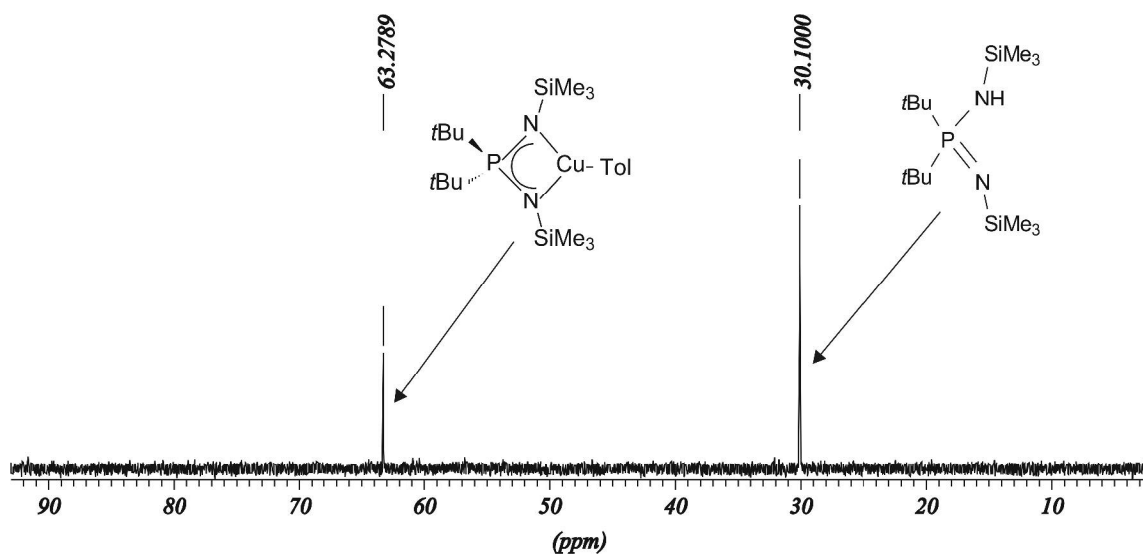
**Figure 3.**  $^{13}\text{C}$  NMR (125.77 MHz,  $\text{THF-d}_8$ , 238 K) spectrum of the **8g**·0.46  $\text{C}_5\text{H}_{12}$ .



**Figure 4.**  $^1\text{H}$  NMR spectrum (500.13 MHz,  $\text{THF-d}_8$ , 298 K) of a mixture of carbene **8g** and an excess of styrene after ca. 2 h at room temperature. Signals marked with a star were assigned to copper styrene complex  $[\text{tBu}_2\text{P}(\text{NSiMe}_3)_2\text{-}\kappa^2\text{N}]\text{Cu}(\eta^2\text{-CH=CHPh})$ , whereas signals  $\text{H}_{\text{a-c}}$  were assigned to three cyclopropane protons.



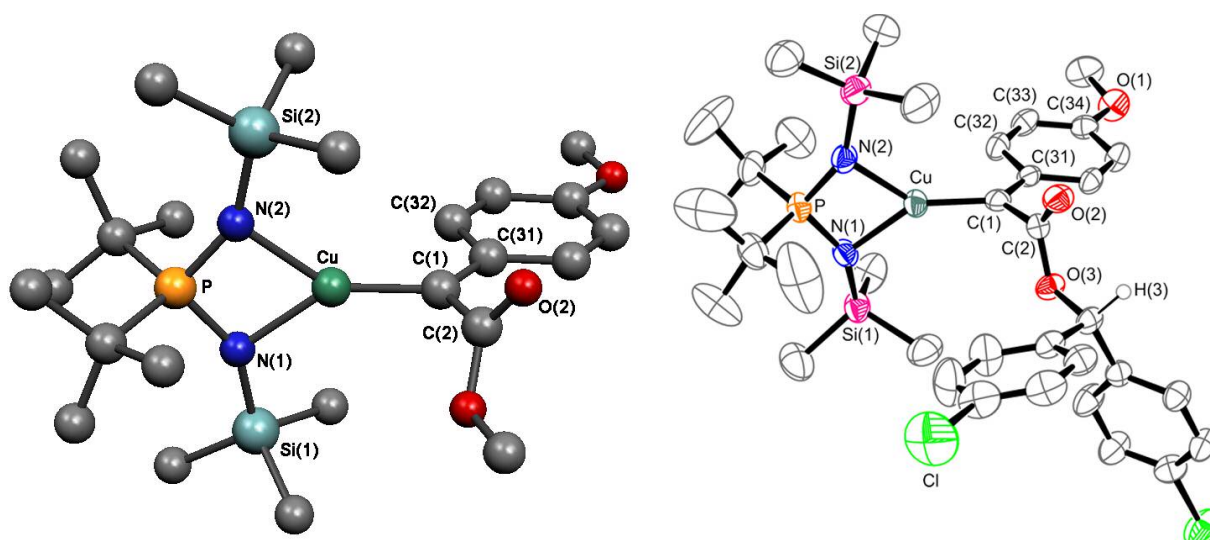
**Figure 5.**  $^{31}\text{P}$  NMR (202.46 MHz, toluene- $d_8$ ) spectrum of **8g** after complete decomposition.



**Figure 6.**  $^{31}\text{P}$  NMR (202.46 MHz, toluene- $d_8$ ) spectrum of  $[\text{tBu}_2\text{P}(\text{NSiMe}_3)_2-\kappa^2\text{M}]\text{Cu}=\text{C}[p\text{-NO}_2\text{-C}_6\text{H}_4]_2$  (**6**) after complete decomposition.

## Calculation part

The calculations were carried out on 56 CPU cluster with Intel Xeon processors (2.66 GHz) with Turbomole (version 5.7)<sup>8</sup> software package. For the DFT calculations, BP86 method (Becke's exchange<sup>9</sup> and Perdew's gradient corrected<sup>10</sup> correlation functional) was utilized. Implemented split-valence SV(P) basis set was employed for geometry optimisation of **8e** with Turbomole program, whereas triple- $\xi$  quality basis TZVP was used for single-point energy calculation on SV(P)-optimised structure of **8e**.



**Figure 7.** Optimized BP86/SV(P) optimized structure of **8e** (left) and X-ray structure of **8g** (right). Selected bond length (Å) and angles (°):

Parameter	X-ray ( <b>8g</b> )	Calculated	Parameter	X-ray ( <b>8g</b> )	Calculated
Cu-C(1)	1.822	1.850	P-Cu-C(1)	177.9	178.2
Cu-N(1)	2.003	2.040	C(1)-Cu-N(2)	142.2	143.3
Cu-N(2)	1.993	2.037	C(1)-Cu-N(1)	140.0	139.6
N-P (av.)	1.606	1.637	Cu-C(1)-C(31)-C(2)	-179.6	174.8
C(1)-C(2)	1.484	1.480	N(2)-Cu-C(1)-C(31)	-95.8	-92.5
C(1)-C(31)	1.434	1.441	N(2)-Cu-C(1)-C(2)	84.6	82.6
C(2)-O(2)	1.202	1.227	Cu-C(1)-C(2)-O(2)	-88.3	107.4
N(2)-Cu-N(1)	77.8	77.0			

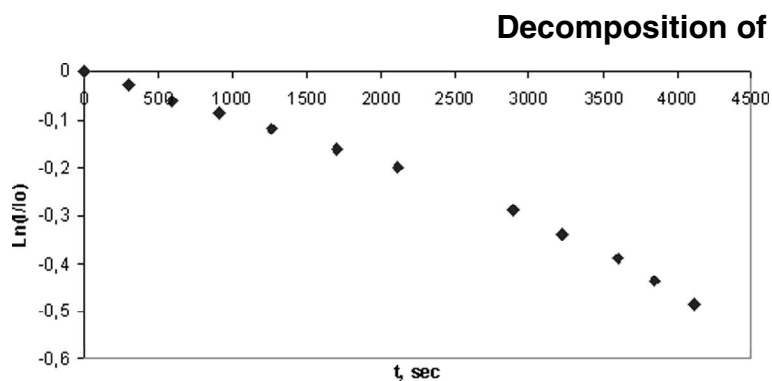
Atomic Cartesian coordinates for the optimized structure of **8e** are given in 1 Å scale:

Cu	-0.0981542	0.0994367	0.4023542
N	1.2702354	-1.3173783	-0.1300648
N	-1.2636716	-1.4625607	-0.1911050
P	0.0655659	-2.3576251	-0.5159180
Si	2.9665378	-0.9558096	0.0685365

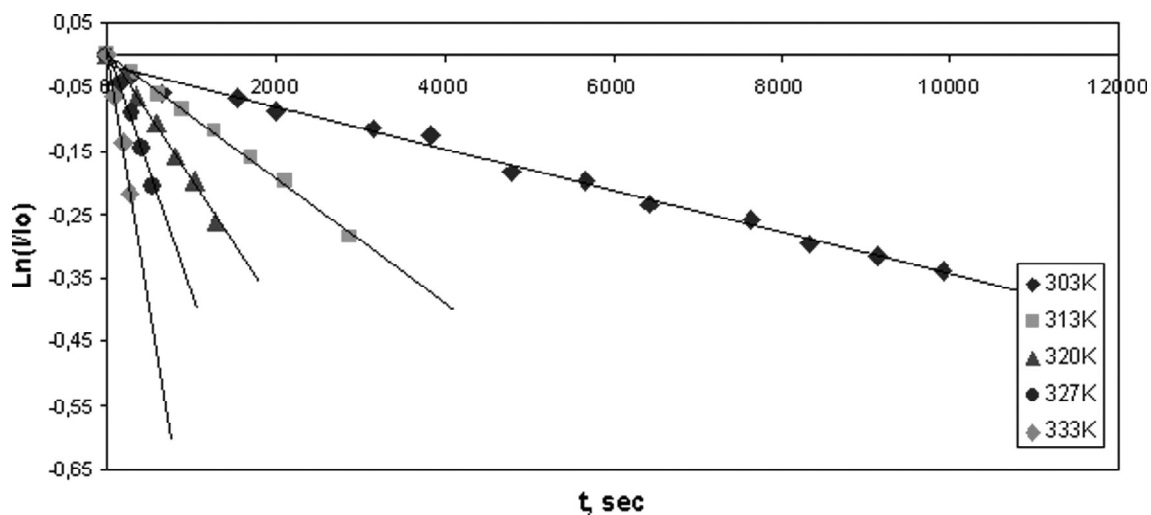
Si	-2.9983858	-1.2683498	-0.1160351
C	-0.1551721	1.8311885	1.0517357
C	-0.3572887	1.8882819	2.5165384
O	-1.4077922	2.2373378	3.0468266
O	0.7122772	1.4333183	3.2291630
C	0.5305571	1.3842402	4.6522620
C	0.1405264	-3.9183175	0.6032209
C	1.5801230	-4.4645926	0.6917604
H	2.2756043	-3.7045750	1.1047963
H	1.9757018	-4.8027522	-0.2880240
H	1.5976995	-5.3435213	1.3780131
C	-0.2879279	-3.4358899	2.0076221
H	0.3301973	-2.5763597	2.3471094
H	-0.1561521	-4.2676553	2.7381243
H	-1.3509075	-3.1183839	2.0264587
C	-0.8133574	-5.0346701	0.1328924
H	-1.8532961	-4.6698636	-0.0025473
H	-0.8436528	-5.8427020	0.9015685
H	-0.4773645	-5.5020302	-0.8171926
C	0.1288361	-2.7948637	-2.3870211
C	-1.2363209	-3.3202285	-2.8769883
H	-1.5346308	-4.2709564	-2.3884832
H	-1.1817624	-3.5137470	-3.9737338
H	-2.0409108	-2.5745747	-2.7066154
C	1.2352186	-3.8139082	-2.7247518
H	2.2274831	-3.4976999	-2.3393073
H	1.3233441	-3.9087245	-3.8325667
H	1.0113274	-4.8275121	-2.3284926
C	0.4284582	-1.4619681	-3.1098335
H	1.4377543	-1.0769279	-2.8553572
H	-0.3150646	-0.6810838	-2.8386760
H	0.3791800	-1.6208659	-4.2121237
C	3.3114142	0.7746655	-0.6416851
H	2.6916578	1.5442749	-0.1302884
H	3.0803224	0.8224274	-1.7303111
H	4.3824367	1.0524615	-0.5104329
C	3.4196178	-0.9181592	1.9161045
H	2.7495744	-0.2055639	2.4471806
H	4.4715968	-0.5839670	2.0687044
H	3.3094768	-1.9148915	2.4009056
C	4.1540844	-2.1520895	-0.8308534
H	4.0439662	-2.0892727	-1.9366019
H	4.0238091	-3.2151508	-0.5327439
H	5.2037799	-1.8662956	-0.5882581
C	-3.5635406	-0.0675290	-1.4823427
H	-3.3735215	-0.4746849	-2.5012082
H	-3.0128801	0.8959729	-1.3962870
H	-4.6524740	0.1546178	-1.4040738
C	-3.4730137	-0.5231851	1.5648914
H	-3.1875761	-1.2040151	2.3988122
H	-4.5735134	-0.3584678	1.6279107
H	-2.9735079	0.4543010	1.7489632
C	-3.9891933	-2.8914082	-0.2906680
H	-3.7985567	-3.5769266	0.5647485

H	-3.7735038	-3.4451233	-1.2302407
H	-5.0781363	-2.6541803	-0.2853939
C	-0.1283111	3.0774828	0.3285408
C	0.0244895	3.0702887	-1.0911697
H	0.0968557	2.0936538	-1.5982463
C	0.0954988	4.2437180	-1.8416945
H	0.2195441	4.1810797	-2.9326118
C	0.0029151	5.4973886	-1.1859266
C	-0.1647371	5.5399591	0.2230871
H	-0.2432020	6.5261017	0.7073688
C	-0.2265883	4.3629200	0.9576730
H	-0.3759232	4.4168828	2.0474113
O	0.0606306	6.6962023	-1.8104379
C	0.2389146	6.7398521	-3.2207132
H	0.2671784	7.8140919	-3.4907461
H	-0.6078415	6.2496070	-3.7548506
H	1.1969741	6.2587589	-3.5254694
H	-0.2843849	0.6782150	4.9208134
H	0.2758251	2.3875408	5.0574202
H	1.4963646	1.0338650	5.0655490

## Kinetic studies with $\alpha$ -carbonyl carbene **8g**



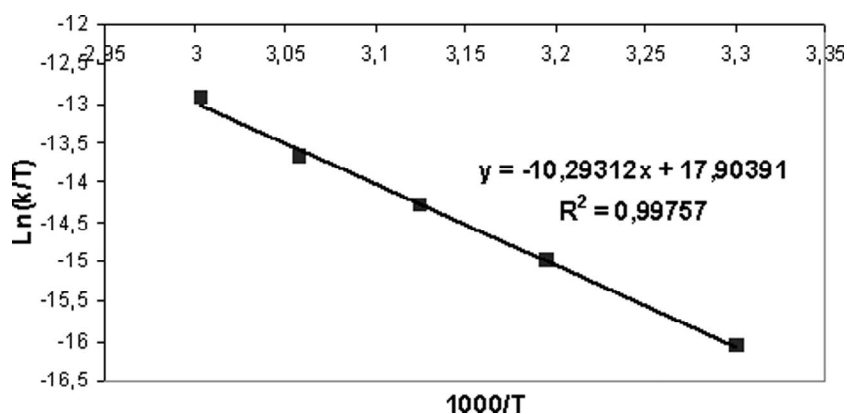
**Figure 8.** . Plot of  $\text{Ln}(I/I_0)$  vs. time for thermal decomposition of carbene **8g** at 313 K (data plot for ca. 40% conversion) showing a deviation from the first order after ca. 20% conversion.



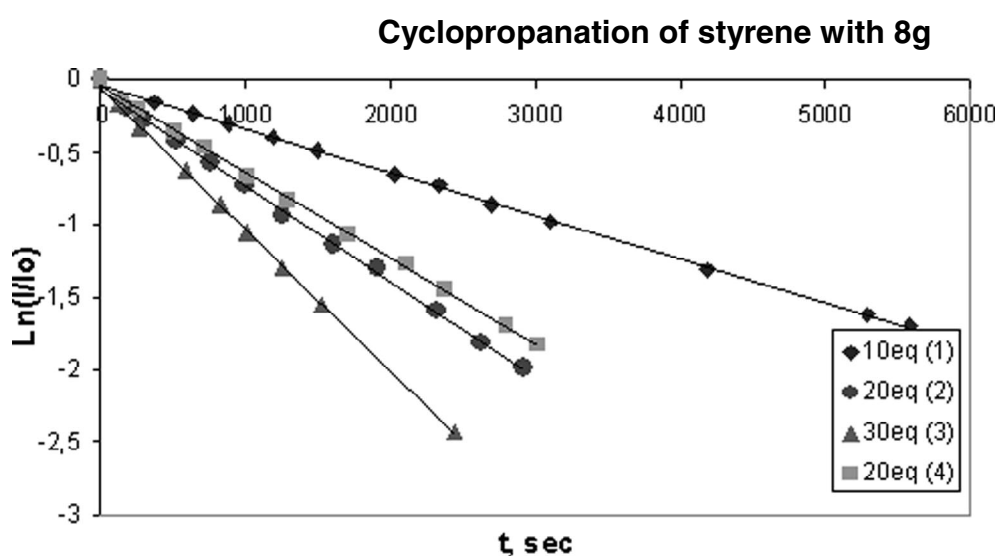
**Figure 9.** Decomposition of carbene **8g** at various temperatures. Data collected for 20-25% conversion.

**Table 1.** Decomposition constants of **43** over a temperature range 303-333 K.

T, K	$k_{\text{dec}}, \text{s}^{-1}$
303	$3,27(9) \times 10^{-5}$
313	$9,71(21) \times 10^{-5}$
320	$2,02(6) \times 10^{-4}$
327	$3,83(24) \times 10^{-4}$
333	$8,09(29) \times 10^{-4}$



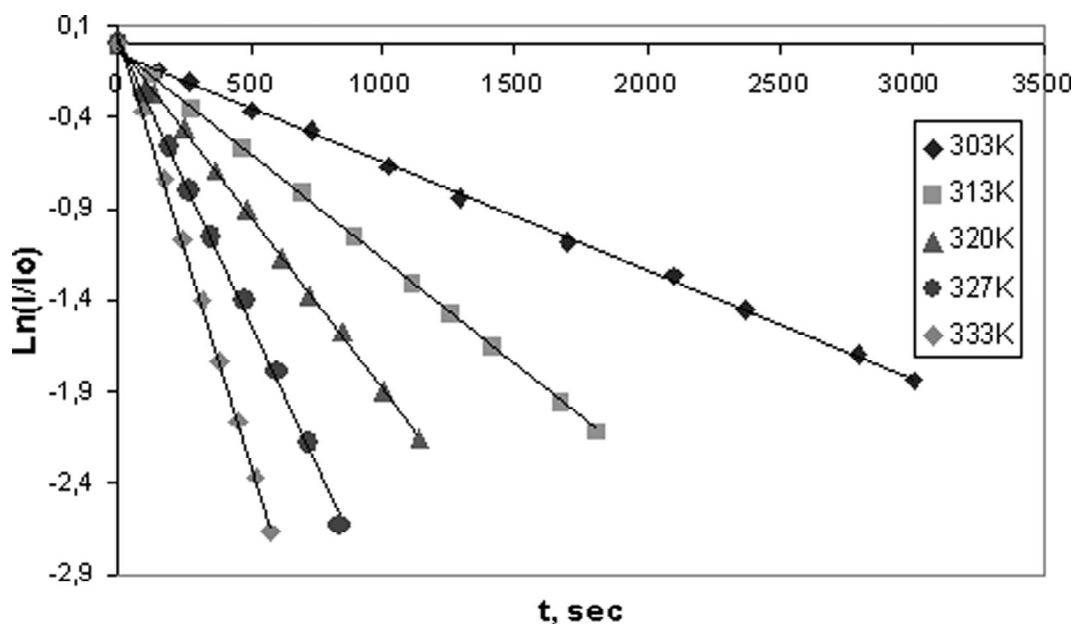
**Figure 10.** Eyring plot for the decomposition of copper carbene **8g** in toluene- $d_8$  over a temperature range 303-333 K.



**Figure 11.** Cyclopropanation of styrene with copper carbene **8g** at various olefin/carbene ratios at 303 K under the pseudo-first order conditions.

**Table 2.** Observed first-order and actual second-order rate constants for styrene cyclopropanation with **8g** at various olefin/carbene ratios at 303 K under the pseudo-first order conditions. (Determination of the reaction order).

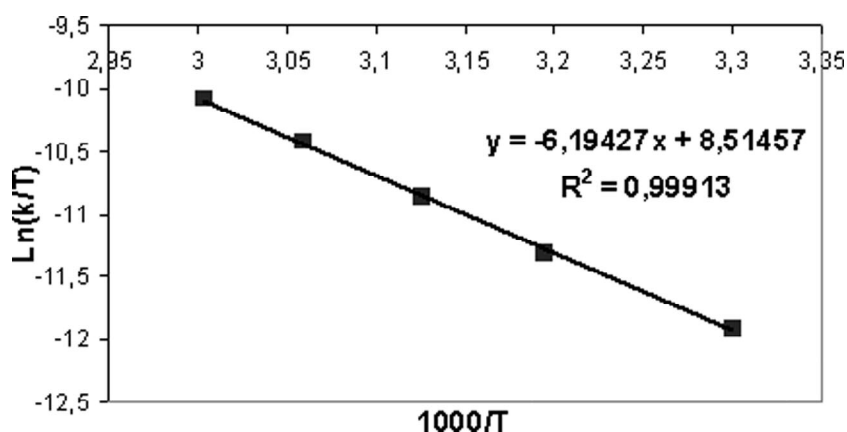
Equiv. Styrene	$C_{\text{carb}} \times 10^{-2}$ mol/l	$C_{\text{olef}} \times 10^{-1}$ mol/l	$k_{\text{obs}} \times 10^{-4}$ $s^{-1}$	$k_{\text{dec}} \times 10^{-5}$ $s^{-1}$	$k_{\text{pseudo}} \times 10^{-4}$ $s^{-1}$	$k_{\text{cyclop}} \times 10^{-3}$ l/(mol $\times$ s)
10 (1)	1.72	1,71(2)	3,01(2)	3,27(9)	2,68(3)	1,57(2)
20 (2)	1.37	2,75(1)	5,94(6)	3,27(9)	5,61(6)	2,04(2)
30 (3)	1.72	5,14(2)	9,86(11)	3,27(9)	9,53(11)	1,85(2)
20 (4)	1.72	3,44(2)	6,63(9)	3,27(9)	6,30(9)	1,84(3)



**Figure 12.** Cyclopropanation of styrene with copper carbene **8g** at various temperatures in toluene- $d_8$  and 1:20 carbene/olefin ratio ( $C_{olef} = 2.75(1) \times 10^{-1}$  M).

**Table 3.** Observed first-order and actual second-order rate constants for styrene cyclopropanation with **8g** over a temperature range 303-333 K at 20:1 olefin/carbene ratio under the pseudo-first order conditions ( $C_{olef} = 2.75(1) \times 10^{-1}$  M).

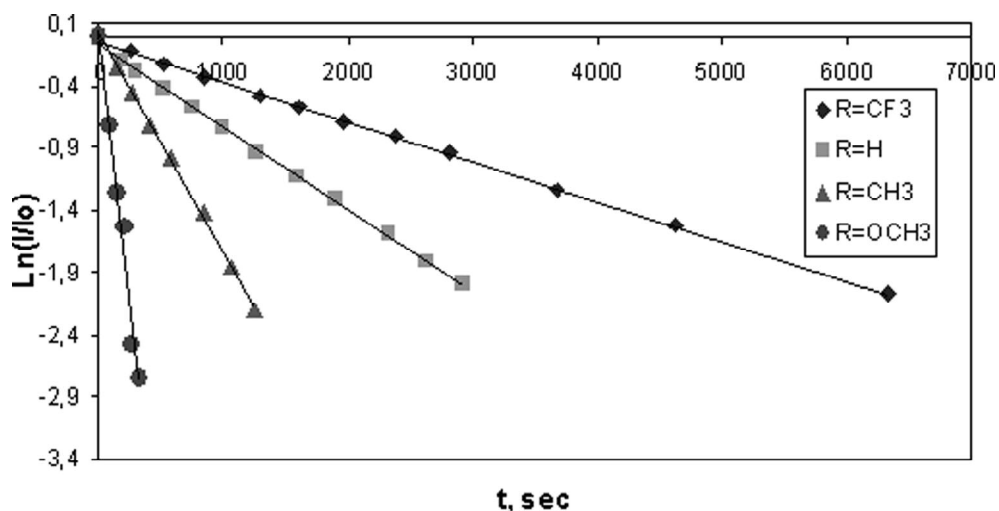
T, K	$k_{obs}$ $s^{-1}$	$k_{dec}$ $s^{-1}$	$k_{pseudo}$ $s^{-1}$	$k_{cyclop}$ $l/(mol \times s)$
303	$5,94(6) \times 10^{-4}$	$3,27(9) \times 10^{-5}$	$5,61(6) \times 10^{-4}$	$2,04(2) \times 10^{-3}$
313	$1,160(4) \times 10^{-3}$	$9,71(21) \times 10^{-5}$	$1,063(5) \times 10^{-3}$	$3,87(2) \times 10^{-3}$
320	$1,89(1) \times 10^{-3}$	$2,02(6) \times 10^{-4}$	$1,69(1) \times 10^{-3}$	$6,14(5) \times 10^{-3}$
327	$3,09(4) \times 10^{-3}$	$3,83(24) \times 10^{-4}$	$2,71(5) \times 10^{-3}$	$9,85(17) \times 10^{-3}$
333	$4,64(4) \times 10^{-3}$	$8,09(29) \times 10^{-4}$	$3,83(5) \times 10^{-3}$	$1,39(2) \times 10^{-2}$



**Figure 13.** Eyring plot for the cyclopropanation of styrene by **8g** in toluene- $d_8$  over the temperature range 303-333 K.



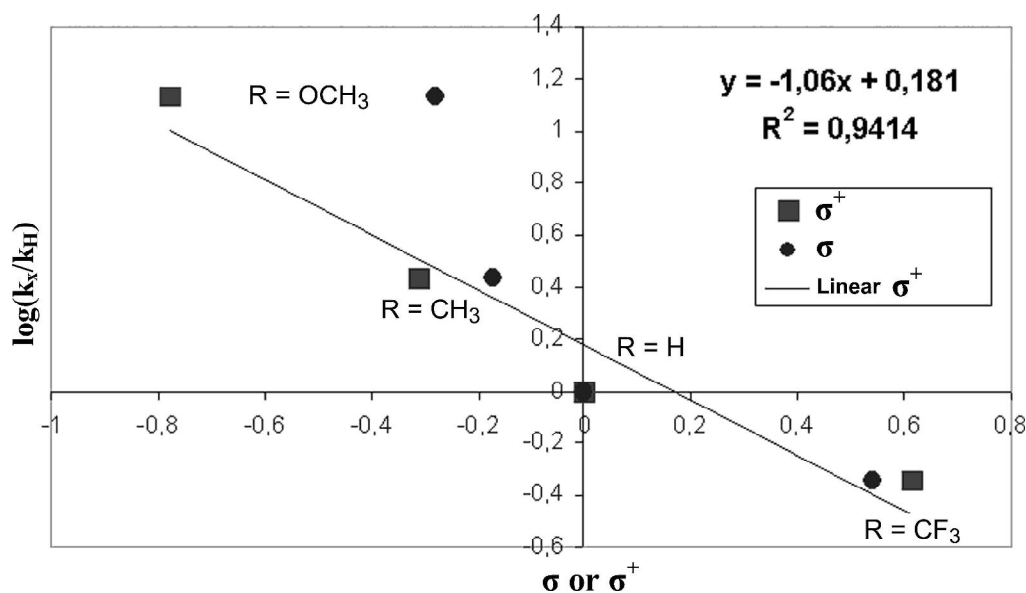
### Cyclopropanation of *p*-substituted styrenes with **8g**



**Figure 14.** Cyclopropanation of *para*-substituted styrenes  $R-C_6H_4CH=CH_2$  by copper carbene **8g** at 303 K and 1:20 carbene/olefin ratio.

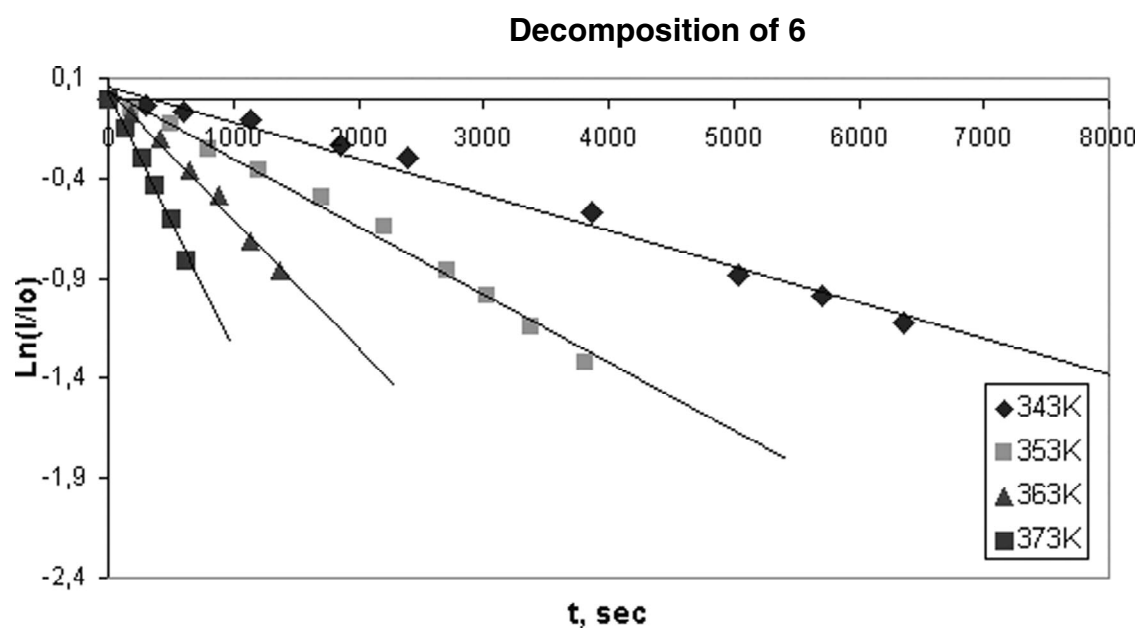
**Table 4.** Observed reaction constants for cyclopropanation of *para*-substituted styrenes  $R-C_6H_4CH=CH_2$  by copper carbene **8g** at 303 K and 1:20 carbene/olefin ratio.

R	$k_{obs} (s^{-1})$	$k_{dec} (s^{-1})$	$k_{pseudo} (s^{-1})$	$k_X/k_H$	$\sigma$	$\sigma^+$
H	$6,63(9) \times 10^{-4}$	$3,27(9) \times 10^{-5}$	$6,30(9) \times 10^{-4}$	1,000	0	0
CF <sub>3</sub>	$3,20(3) \times 10^{-4}$	$3,27(9) \times 10^{-5}$	$2,87(3) \times 10^{-4}$	0,4559	0,54	0,612
CH <sub>3</sub>	$1,75(2) \times 10^{-3}$	$3,27(9) \times 10^{-5}$	$1,72(2) \times 10^{-3}$	2,725	-0,17	-0,311
OCH <sub>3</sub>	$8,64(56) \times 10^{-3}$	$3,27(9) \times 10^{-5}$	$8,61(56) \times 10^{-3}$	13,661	-0,28	-0,778



**Figure 15.** Hammett plot of cyclopropanation of *para*-substituted styrenes with copper(I) carbene **8g**.

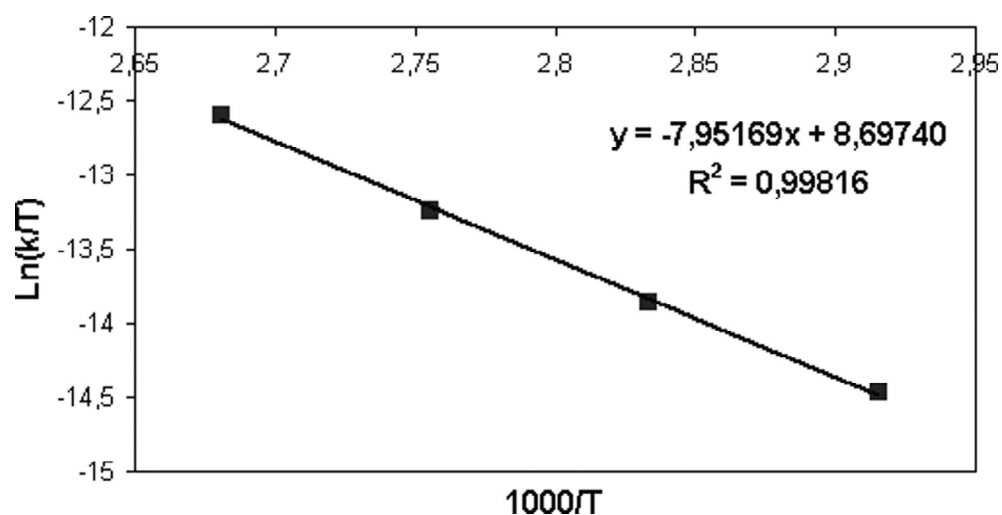
## Kinetic studies with diarylcarbene 6



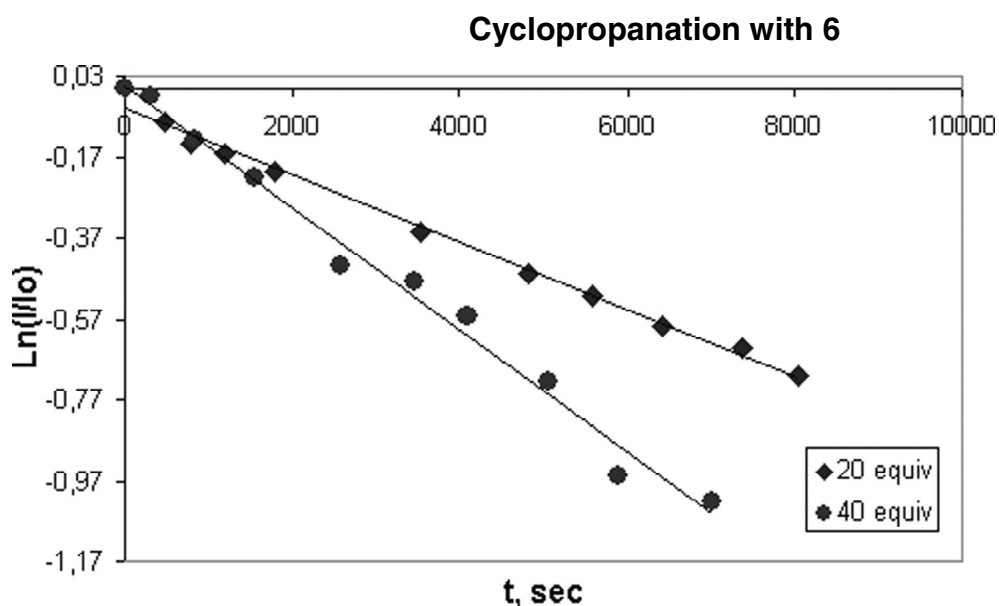
**Figure 16.** Decomposition of carbene **6** in toluene- $d_8$  over a temperature range 343-373 K. The data were collected for ca. 1.5 half-lives.  $C_{\text{carbene}} = 1.56 \times 10^{-2}$  M

**Table 5.** Observed first-order rate constants of decomposition of **6** in toluene- $d_8$  over a temperature range 343-373 K.

T, K	$k_{\text{dec}} (\text{s}^{-1})$
343	$1,80(7) \times 10^{-4}$
353	$3,40(10) \times 10^{-4}$
363	$6,44(26) \times 10^{-4}$
373	$1,27(5) \times 10^{-3}$



**Figure 17.** Eyring plot for the decomposition of copper carbene **6** in toluene- $d_8$  over a temperature range 343-373 K.

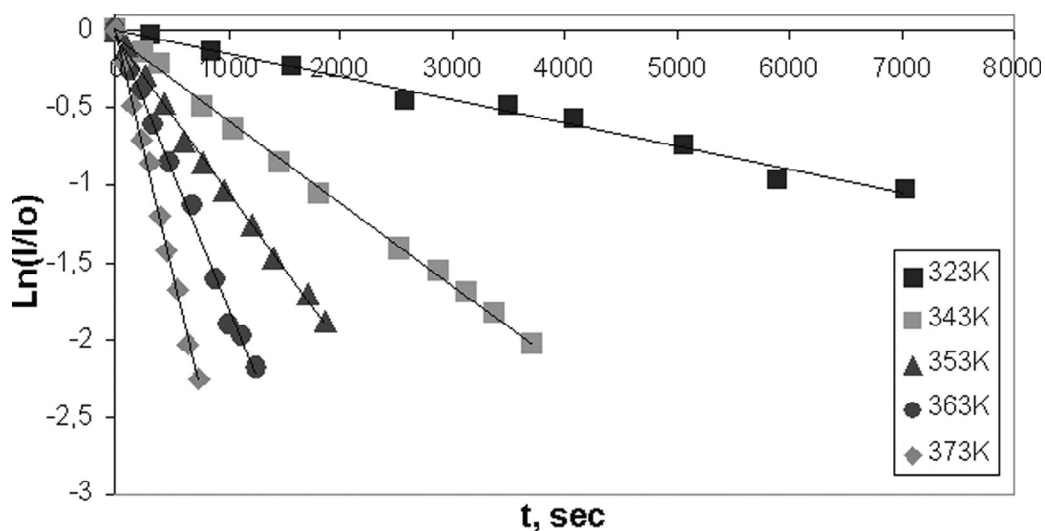


**Figure 18.** Cyclopropanation of styrene with carbene **6** at different carbene/olefin ratios at 323 K.

**Table 6.** Observed first-order and actual second-order rate constants for styrene cyclopropanation with **6** at various olefin/carbene ratios at 323 K under the pseudo-first order conditions. (Determination of the reaction order).

Equiv. styrene	$C_{\text{carb}} \times 10^{-2}$ mol/l	$C_{\text{olef}} \times 10^{-1}$ mol/l	$k_{\text{obs}} \times 10^{-5}$ $\text{s}^{-1}$	$^a k_{\text{dec}} \times 10^{-5}$ $\text{s}^{-1}$	$k_{\text{pseudo}} \times 10^{-5}$ $\text{s}^{-1}$	$k_{\text{cyclop}} \times 10^{-4}$ $\text{l}/(\text{mol} \times \text{s})$
20	1.56	3.13(2)	8,33(23)	3,93(16)	4,40(28)	1,41(9)
40	1.56	6.26(2)	15,1(6)	3,93(16)	11,2(6)	1,79(10)

<sup>a</sup> obtained by extrapolation of the Eyring plot depicted in Figure 17.

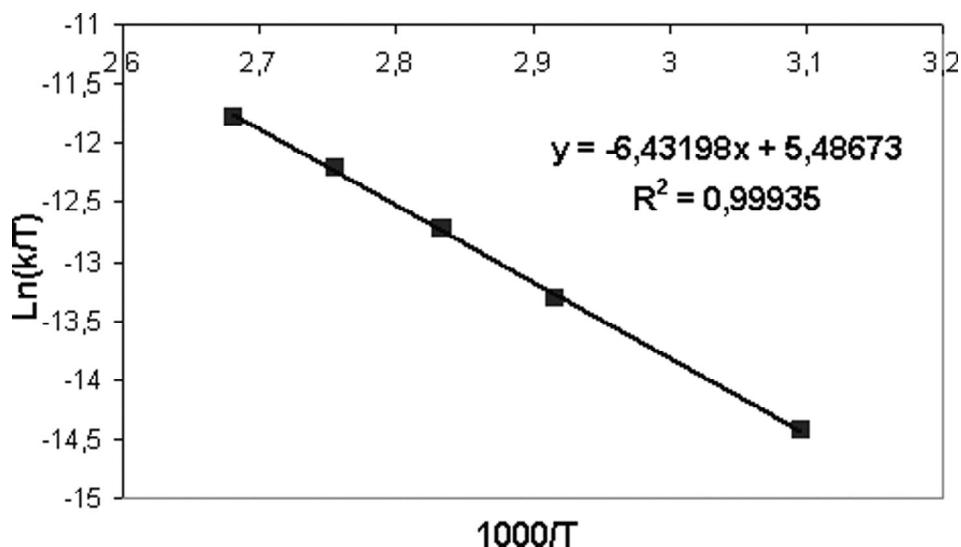


**Figure 19.** Cyclopropanation of styrene with carbene **6** over a temperature range 323-373 K at 1:40 carbene/olefin ratio under the pseudo-first order conditions ( $C_{\text{olef}} = 6.26(2) \times 10^{-1} \text{ M}$ ).

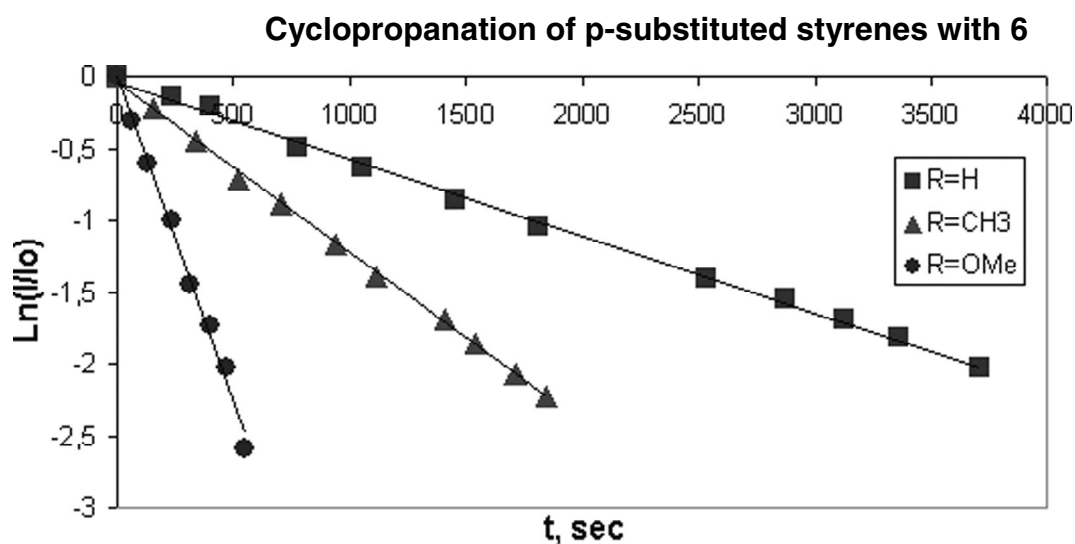
**Table 7.** Observed first-order and actual second-order rate constants for styrene cyclopropanation with **6** over a temperature range 303–333 K at 40:1 olefin/carbene ratio under the pseudo-first order conditions ( $C_{\text{olef}} = 6.26(2) \times 10^{-1}$  M).

T, K	$k_{\text{obs}}$ $\text{s}^{-1}$	$k_{\text{dec}}$ $\text{s}^{-1}$	$k_{\text{pseudo}}$ $\text{s}^{-1}$	$k_{\text{cyclop}}$ $\text{l}/(\text{mol} \times \text{s})$
323 <sup>a</sup>	$1,51(6) \times 10^{-4}$	$3,93(16) \times 10^{-5}$	$1,11(6) \times 10^{-4}$	$1,78(10) \times 10^{-4}$
343	$5,37(8) \times 10^{-4}$	$1,80(7) \times 10^{-4}$	$3,57(11) \times 10^{-4}$	$5,71(17) \times 10^{-4}$
353	$9,995(75) \times 10^{-4}$	$3,40(10) \times 10^{-4}$	$6,60(12) \times 10^{-4}$	$1,06(2) \times 10^{-3}$
363	$1,78(4) \times 10^{-3}$	$6,44(26) \times 10^{-4}$	$1,13(5) \times 10^{-3}$	$1,81(8) \times 10^{-3}$
373	$3,08(5) \times 10^{-3}$	$1,27(5) \times 10^{-3}$	$1,81(8) \times 10^{-3}$	$2,89(12) \times 10^{-3}$

<sup>a</sup>  $k_{\text{dec}}$  at 323 K was obtained by extrapolation of the Eyring plot depicted in Figure 17.



**Figure 20.** Eyring plot for the cyclopropanation of styrene by **6** over a temperature range 323–373 K in toluene- $d_8$ .

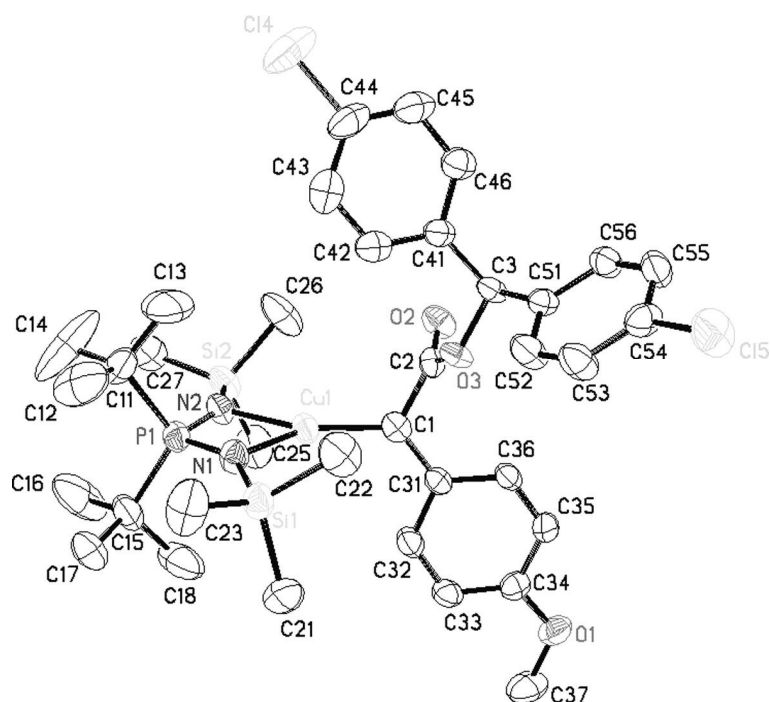


**Figure 21.** Cyclopropanation of para-substituted styrenes  $R\text{-C}_6\text{H}_4\text{CH=CH}_2$  by copper carbene **6** at 343 K and 1:40 carbene/olefin ratio.

**Table 8.** Observed reaction constants for cyclopropanation of *para*-substituted styrenes R-C<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> by copper carbene **6** at 343 K and 1:40 carbene/olefin ratio.

R	k <sub>obs</sub> (s <sup>-1</sup> )	k <sub>dec</sub> (s <sup>-1</sup> )	k <sub>pseudo</sub> (s <sup>-1</sup> )	k <sub>X</sub> /k <sub>H</sub>	σ	σ <sup>+</sup>
H	5,37(8) × 10 <sup>-4</sup>	1,80(7) × 10 <sup>-4</sup>	3,57(11) × 10 <sup>-4</sup>	1,00	0	0
CH <sub>3</sub>	1,18(1) × 10 <sup>-3</sup>	1,80(7) × 10 <sup>-4</sup>	1,00(2) × 10 <sup>-3</sup>	2,808	-0,17	-0,311
OCH <sub>3</sub>	4,47(14) × 10 <sup>-3</sup>	1,80(7) × 10 <sup>-4</sup>	4,29(14) × 10 <sup>-3</sup>	12,02	-0,28	-0,778

### Complete list of bond length and angles of 8g



**Figure 22.** ORTEP plot of **8g**, hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°):

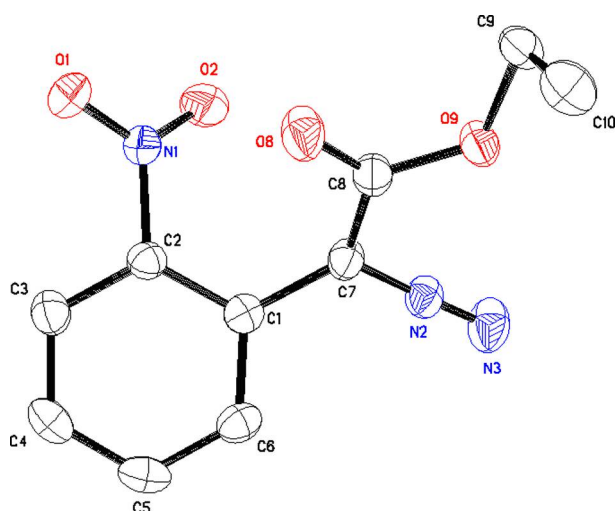
Cu11-C11	1.825(4)	C321-C331	1.377(6)
Cu11-N21	2.000(3)	C331-C341	1.401(6)
Cu11-N11	2.002(3)	C341-O11	1.348(5)
Cu11-P11	2.5561(12)	C341-C351	1.401(6)
N11-P11	1.606(3)	C351-C361	1.357(5)
N11-Si11	1.706(3)	O11-C371	1.442(5)
N21-P11	1.604(3)	C411-C421	1.360(6)
N21-Si21	1.698(3)	C411-C461	1.383(6)
P11-C151	1.858(5)	C421-C431	1.390(7)
P11-C111	1.874(5)	C431-C441	1.386(7)
Si11-C221	1.867(5)	C441-C451	1.354(7)
Si11-C231	1.874(5)	C451-C461	1.380(6)
Si11-C211	1.881(5)	C511-C521	1.378(6)
Si21-C251	1.855(5)	C511-C561	1.379(5)
Si21-C261	1.869(5)	C521-C531	1.388(6)
Si21-C271	1.875(5)	C531-C541	1.370(6)
Cl41-C441	1.739(5)	C541-C551	1.364(6)
Cl51-C541	1.758(4)	C551-C561	1.377(6)
C11-C311	1.431(5)	Cu12-C12	1.819(4)
C11-C21	1.484(6)	Cu12-N12	1.986(3)
C21-O21	1.200(5)	Cu12-N22	2.002(3)
C21-O31	1.356(5)	Cu12-P12	2.5579(12)
O31-C31	1.460(4)	N12-P12	1.601(3)
C31-C411	1.511(5)	N12-Si12	1.708(3)
C31-C511	1.513(5)	N22-P12	1.610(3)
C111-C131	1.490(8)	N22-Si22	1.694(3)
C111-C141	1.510(8)	P12-C152	1.858(5)
C111-C121	1.521(7)	P12-C112	1.860(4)
C151-C161	1.524(7)	Si12-C222	1.855(5)
C151-C171	1.535(6)	Si12-C212	1.863(5)
C151-C181	1.538(7)	Si12-C232	1.878(5)
C311-C321	1.412(5)	Si22-C252	1.847(7)
C311-C361	1.416(5)	Si22-C262	1.847(7)
		Si22-C272	1.856(5)

Cl42-C442	1.756(5)	P11-N21-Si21	150.3(2)
Cl52-C542	1.739(4)	P11-N21-Cu11	89.64(15)
C12-C312	1.437(5)	Si21-N21-Cu11	119.79(18)
C12-C22	1.485(6)	N21-P11-N11	103.02(17)
C22-O22	1.203(4)	N21-P11-C151	109.9(2)
C22-O32	1.350(5)	N11-P11-C151	111.1(2)
O32-C32	1.467(4)	N21-P11-C111	109.7(2)
C32-C512	1.505(5)	N11-P11-C111	109.0(2)
C32-C412	1.512(6)	C151-P11-C111	113.6(2)
C112-C122	1.521(6)	N21-P11-Cu11	51.49(12)
C112-C132	1.532(7)	N11-P11-Cu11	51.56(12)
C112-C142	1.559(7)	C151-P11-Cu11	122.80(16)
C152-C172	1.523(6)	C111-P11-Cu11	123.60(17)
C152-C162	1.532(7)	N11-Si11-C221	108.2(2)
C152-C182	1.534(7)	N11-Si11-C231	116.2(2)
C312-C362	1.410(5)	C221-Si11-C231	106.6(3)
C312-C322	1.424(5)	N11-Si11-C211	111.4(2)
C322-C332	1.363(6)	C221-Si11-C211	108.3(2)
C332-C342	1.402(6)	C231-Si11-C211	105.9(3)
C342-O12	1.358(5)	N21-Si21-C251	109.9(2)
C342-C352	1.384(6)	N21-Si21-C261	108.3(2)
C352-C362	1.377(5)	C251-Si21-C261	109.1(3)
O12-C372	1.441(5)	N21-Si21-C271	115.4(2)
C412-C422	1.358(6)	C251-Si21-C271	108.6(2)
C412-C462	1.389(6)	C261-Si21-C271	105.4(2)
C422-C432	1.392(7)	C311-C11-C21	114.5(3)
C432-C442	1.355(8)	C311-C11-Cu11	128.0(3)
C442-C452	1.368(7)	C21-C11-Cu11	117.5(3)
C452-C462	1.370(6)	O21-C21-O31	123.2(4)
C512-C562	1.383(6)	O21-C21-C11	125.1(4)
C512-C522	1.393(6)	O31-C21-C11	111.7(3)
C522-C532	1.379(6)	C21-O31-C31	116.7(3)
C532-C542	1.380(6)	O31-C31-C411	109.9(3)
C542-C552	1.371(6)	O31-C31-C511	107.1(3)
C552-C562	1.394(6)	C411-C31-C511	111.7(3)
C68-C65#1	1.84(5)	C131-C111-C141	109.5(6)
C68-C64#1	1.91(5)	C131-C111-C121	108.8(5)
C68-C74	1.92(5)	C141-C111-C121	107.3(5)
C60-C81	1.47(4)	C131-C111-P11	106.2(4)
C60-O60	1.65(4)	C141-C111-P11	112.5(4)
O60-C71	1.76(4)	C121-C111-P11	112.4(3)
C67-C65	1.62(3)	C161-C151-C171	109.5(4)
C61-C71	1.89(5)	C161-C151-C181	108.2(5)
C64-C84	1.51(6)	C171-C151-C181	106.8(4)
C64-C83#2	1.76(4)	C161-C151-P11	113.7(4)
C64-C68#3	1.91(5)	C171-C151-P11	112.6(3)
C65-C68#3	1.84(5)	C181-C151-P11	105.6(3)
C71-C76	1.87(3)	C321-C311-C361	115.8(4)
C72-C76	1.37(3)	C321-C311-C11	120.4(4)
C72-C73	1.96(2)	C361-C311-C11	123.8(4)
C73-C75	1.77(2)	C331-C321-C311	123.0(4)
C75-C76	1.92(3)	C321-C331-C341	118.6(4)
C83-C64#2	1.76(4)	O11-C341-C331	124.3(4)
C83-C84	1.81(5)	O11-C341-C351	115.7(4)
C11-Cu11-N21	142.43(15)	C331-C341-C351	119.9(4)
C11-Cu11-N11	139.77(15)	C361-C351-C341	120.2(4)
N21-Cu11-N11	77.76(13)	C351-C361-C311	122.3(4)
C11-Cu11-P11	177.26(13)	C341-O11-C371	118.8(4)
N21-Cu11-P11	38.87(9)	C421-C411-C461	118.3(4)
N11-Cu11-P11	38.91(10)	C421-C411-C31	122.6(4)
P11-N11-Si11	149.5(2)	C461-C411-C31	119.0(4)
P11-N11-Cu11	89.53(15)	C411-C421-C431	121.1(5)
Si11-N11-Cu11	119.48(18)	C441-C431-C421	118.9(5)

C451-C441-C431	120.9(5)	C132-C112-C142	108.3(4)
C451-C441-C141	120.2(4)	C122-C112-P12	112.0(3)
C431-C441-C141	118.9(5)	C132-C112-P12	106.1(3)
C441-C451-C461	119.0(5)	C142-C112-P12	112.7(4)
C451-C461-C411	121.7(4)	C172-C152-C162	108.1(4)
C521-C511-C561	118.8(4)	C172-C152-C182	110.0(4)
C521-C511-C31	121.8(4)	C162-C152-C182	106.7(4)
C561-C511-C31	119.4(4)	C172-C152-P12	113.5(3)
C511-C521-C531	120.9(4)	C162-C152-P12	105.8(3)
C541-C531-C521	118.5(4)	C182-C152-P12	112.4(3)
C551-C541-C531	121.8(4)	C362-C312-C322	116.0(4)
C551-C541-C151	119.4(4)	C362-C312-C12	123.5(3)
C531-C541-C151	118.8(3)	C322-C312-C12	120.5(3)
C541-C551-C561	119.0(4)	C332-C322-C312	121.8(4)
C551-C561-C511	121.0(4)	C322-C332-C342	120.3(4)
C12-Cu12-N12	142.03(15)	O12-C342-C352	124.9(4)
C12-Cu12-N22	140.24(15)	O12-C342-C332	115.4(3)
N12-Cu12-N22	77.72(13)	C352-C342-C332	119.7(4)
C12-Cu12-P12	178.51(13)	C362-C352-C342	119.8(4)
N12-Cu12-P12	38.73(9)	C352-C362-C312	122.4(4)
N22-Cu12-P12	38.99(9)	C342-O12-C372	117.9(3)
P12-N12-Si12	150.2(2)	C422-C412-C462	118.6(4)
P12-N12-Cu12	90.33(15)	C422-C412-C32	123.5(4)
Si12-N12-Cu12	119.37(18)	C462-C412-C32	117.9(4)
P12-N22-Si22	152.0(2)	C412-C422-C432	120.5(5)
P12-N22-Cu12	89.49(15)	C442-C432-C422	119.4(5)
Si22-N22-Cu12	118.18(18)	C432-C442-C452	121.4(5)
N12-P12-N22	102.44(17)	C432-C442-C142	119.8(5)
N12-P12-C152	110.0(2)	C452-C442-C142	118.8(4)
N22-P12-C152	111.3(2)	C442-C452-C462	118.6(5)
N12-P12-C112	111.37(19)	C452-C462-C412	121.4(4)
N22-P12-C112	109.2(2)	C562-C512-C522	118.7(4)
C152-P12-C112	112.1(2)	C562-C512-C32	119.3(4)
N12-P12-Cu12	50.93(12)	C522-C512-C32	122.0(4)
N22-P12-Cu12	51.52(12)	C532-C522-C512	121.4(4)
C152-P12-Cu12	123.40(15)	C522-C532-C542	118.9(4)
C112-P12-Cu12	124.48(16)	C552-C542-C532	121.1(4)
N12-Si12-C222	109.1(2)	C552-C542-C152	119.4(3)
N12-Si12-C212	109.9(2)	C532-C542-C152	119.4(3)
C222-Si12-C212	107.4(2)	C542-C552-C562	119.7(4)
N12-Si12-C232	114.55(19)	C512-C562-C552	120.3(4)
C222-Si12-C232	106.1(2)	C65#1-C68-C64#1	82(3)
C212-Si12-C232	109.5(2)	C65#1-C68-C74	103(3)
N22-Si22-C252	109.2(2)	C64#1-C68-C74	124(3)
N22-Si22-C262	108.2(3)	C81-C60-O60	177(4)
C252-Si22-C262	108.8(5)	C60-O60-C71	77(2)
N22-Si22-C272	117.3(2)	C84-C64-C83#2	104(5)
C252-Si22-C272	105.9(3)	C84-C64-C68#3	133(6)
C262-Si22-C272	107.2(4)	C83#2-C64-C68#3	117(4)
C312-C12-C22	114.2(3)	C67-C65-C68#3	105(3)
C312-C12-Cu12	128.2(3)	O60-C71-C76	91(2)
C22-C12-Cu12	117.5(3)	O60-C71-C61	101(3)
O22-C22-O32	123.3(4)	C76-C71-C61	167(3)
O22-C22-C12	124.8(4)	C76-C72-C73	92.0(19)
O32-C22-C12	111.9(3)	C75-C73-C72	85.8(14)
C22-O32-C32	116.5(3)	C73-C75-C76	82.3(16)
O32-C32-C512	107.0(3)	C72-C76-C71	103(2)
O32-C32-C412	110.5(3)	C72-C76-C75	100(2)
C512-C32-C412	112.6(3)	C71-C76-C75	156(2)
C122-C112-C132	109.3(4)	C64#2-C83-C84	162(3)
C122-C112-C142	108.3(4)	C64-C84-C83	94(4)



## Structural data for ethyl 2-(*o*-nitrophenyl)-2-diazoacetate

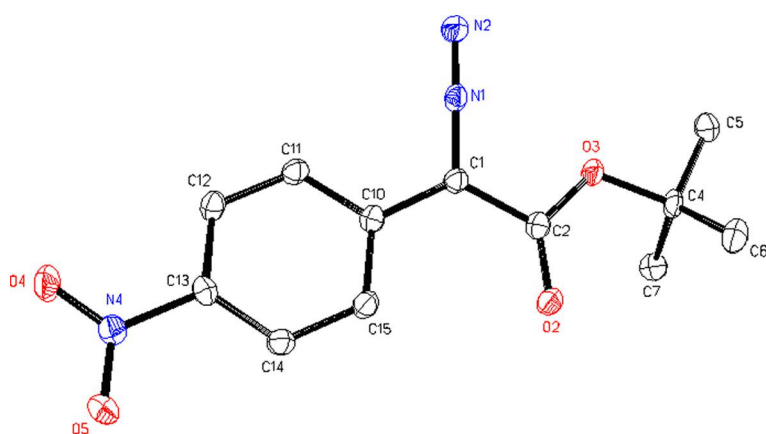


**Figure 23.** ORTEP plot of ethyl 2-(*o*-nitrophenyl)-2-diazoacetate. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)-C(7) 1.4686(18), C(7)-N(2) 1.3229(16), N(2)-N(3) 1.1224(15), C(7)-C(8) 1.4551(18), C(8)-O(8) 1.2104(16), C(8)-O(9) 1.3409(15).

**Table 9.** Crystal data and structure refinement for ethyl 2-(*o*-nitrophenyl)-2-diazoacetate.

Identification code	ivsh2
Empirical formula	C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O <sub>4</sub>
Formula weight	235.20
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Z	4
Unit cell dimensions	a = 8.6002(4) Å      α = 90 deg. b = 8.4637(4) Å      β = 98.119(1) deg. c = 14.9375(6) Å      γ = 90 deg.
Volume	1076.40(8) Å <sup>3</sup>
Density (calculated)	1.45 g/cm <sup>3</sup>
Absorption coefficient	0.12 mm <sup>-1</sup>
Crystal shape	polyhedron
Crystal size	0.44 x 0.22 x 0.05 mm <sup>3</sup>
Theta range for data collection	2.4 to 27.5 deg.
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected	10798
Independent reflections	2466 (R(int) = 0.0334)
Observed reflections	1837 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.95
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2466 / 0 / 155
Goodness-of-fit on F <sup>2</sup>	1.04
Final R indices (I > 2σ(I))	R1 = 0.036, wR2 = 0.079
Largest diff. peak and hole	0.20 and -0.19 eÅ <sup>-3</sup>

## Structural data for 7b

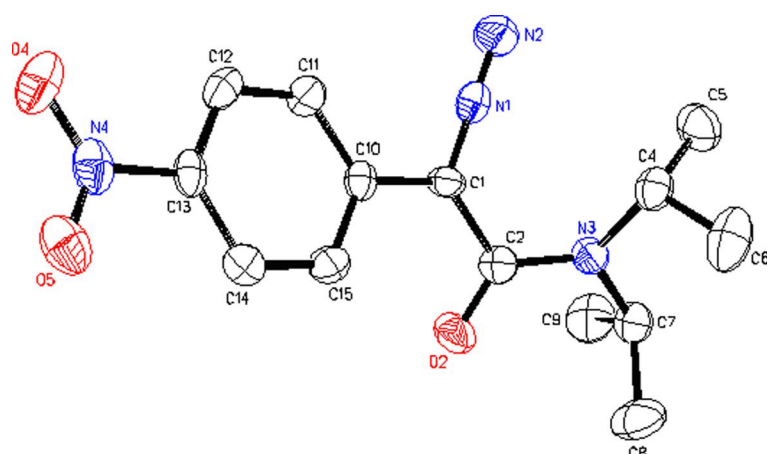


**Figure 24.** ORTEP plot of **7b**. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): O(2)-C(2) 1.207(2), O(3)-C(2) 1.343(2), O(4)-N(4) 1.228(2), O(5)-N(4) 1.226(2), N(1)-N(2) 1.121(2), N(1)-C(1) 1.329(3), N(4)-C(13) 1.462(2), C(1)-C(10) 1.460(3), C(1)-C(2) 1.470(3).

**Table 10.** Crystal data and structure refinement for **7b**.

Identification code	ivsh10
Empirical formula	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub>
Formula weight	263.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
Z	4
Unit cell dimensions	a = 9.067(3) Å      α = 90.0 deg. b = 12.732(4) Å      β = 97.935(7) deg. c = 10.946(3) Å      γ = 90.0 deg.
Volume	1251.6(7) Å <sup>3</sup>
Density (calculated)	1.40 g/cm <sup>3</sup>
Absorption coefficient	0.11 mm <sup>-1</sup>
Crystal shape	irregular
Crystal size	0.27 x 0.14 x 0.05 mm <sup>3</sup>
Theta range for data collection	2.3 to 28.3 deg.
Index ranges	-9 ≤ h ≤ 11, -5 ≤ k ≤ 15, -14 ≤ l ≤ 4
Reflections collected	3139
Independent reflections	2533 (R(int) = 0.0195)
Observed reflections	2052 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2533 / 0 / 224
Goodness-of-fit on F <sup>2</sup>	1.07
Final R indices (I > 2σ(I))	R1 = 0.054, wR2 = 0.123
Largest diff. peak and hole	0.37 and -0.25 eÅ <sup>-3</sup>

## Structural data for 7d

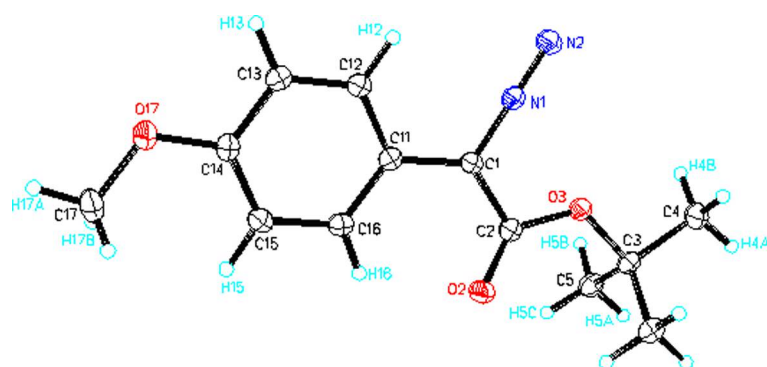


**Figure 25.** ORTEP plot of **7d**. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)-N(1) 1.323(4), C(1)-C(10) 1.452(4), C(1)-C(2) 1.497(5), N(1)-N(2) 1.138(4), C(2)-O(2) 1.226(4), C(2)-N(3) 1.364(4), N(4)-O(5) 1.232(4), N(4)-O(4) 1.237(4), N(4)-C(13) 1.465(4).

**Table 11.** Crystal data and structure refinement for **7d**.

Identification code	ivsh8
Empirical formula	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>
Formula weight	290.32
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Z	8
Unit cell dimensions	a = 18.164(3) Å      α = 90 deg. b = 12.3328(19) Å    β = 102.993(5) deg. c = 13.978(3) Å      γ = 90 deg.
Volume	3051.2(9) Å <sup>3</sup>
Density (calculated)	1.26 g/cm <sup>3</sup>
Absorption coefficient	0.09 mm <sup>-1</sup>
Crystal shape	polyhedron
Crystal size	0.22 x 0.22 x 0.08 mm <sup>3</sup>
Theta range for data collection	2.0 to 21.5 deg.
Index ranges	-15 ≤ h ≤ 18, -12 ≤ k ≤ 12, -12 ≤ l ≤ 14
Reflections collected	9603
Independent reflections	3493 (R(int) = 0.0685)
Observed reflections	1925 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.98
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3493 / 0 / 387
Goodness-of-fit on F <sup>2</sup>	0.94
Final R indices (I > 2σ(I))	R1 = 0.044, wR2 = 0.078
Largest diff. peak and hole	0.16 and -0.23 eÅ <sup>-3</sup>

## Structural data for 7f



**Figure 26.** ORTEP plot of **7f**. Selected bond lengths (Å) and angles (°): C(1)-N(1) 1.3188(17), C(1)-C(2) 1.4679(18), C(2)-O(2) 1.2069(16), C(2)-O(3) 1.3487(15), N(1)-N(2) 1.1268(17), C(1)-C(11) 1.4667(18), C(14)-O(17) 1.3726(16).

**Table 12.** Crystal data and structure refinement for **7f**.

Identification code	ivsh19
Empirical formula	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>
Formula weight	248.28
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pnma
Z	4
Unit cell dimensions	a = 8.5078(8) Å      α = 90 deg. b = 6.7786(6) Å      β = 90 deg. c = 21.9080(19) Å    γ = 90 deg.
Volume	1263.5(2) Å <sup>3</sup>
Density (calculated)	1.30 g/cm <sup>3</sup>
Absorption coefficient	0.09 mm <sup>-1</sup>
Crystal shape	polyhedron
Crystal size	0.48 x 0.14 x 0.12 mm <sup>3</sup>
Theta range for data collection	1.9 to 28.3 deg.
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	12568
Independent reflections	1703 (R(int) = 0.0235)
Observed reflections	1489 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.96
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1703 / 0 / 144
Goodness-of-fit on F <sup>2</sup>	1.06
Final R indices (I > 2σ(I))	R1 = 0.037, wR2 = 0.096
Largest diff. peak and hole	0.32 and -0.26 eÅ <sup>-3</sup>

## References

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- (1) M. Regitz, *Chem. Ber.* **1965**, 1210.
  - (2) T.G. Curphey, *Org. Prep. Proced. Int.* **1981**, 13(2), 112.
  - (3) R. E. Harmon, G. Wellman and S.K. Gupta, *J. Org. Chem.* **1973**, 38, 11.
  - (4) B.F. Straub, F. Eisenträger and P. Hofmann, *Chem. Commun.* **1999**, 2507.
  - (5) K. A. Connors, *Chemical Kinetics*, VCH Publishes, 1990.
  - (6) Prepared by modified method of L. Lombardo and L.N. Mander, *Synthesis*, **1980**, 368.
  - (7) Prepared by modified method: B. Neises and W. Steglich, *Org. Synth. Coll.* **1992**, 70, 93.
  - (8) (a) Eichkorn, K.; Treutler, O.; Oehm, H.; Haeser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 240, 283; (b) Eichkorn, K.; Treutler, O.; Oehm, H.; Haeser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 242, 652; (c) Ahlrichs, R.; Baer, M.; Haeser, M.; Horn, H.; Koelmel, C. *Chem. Phys. Lett.* **1989**, 162, 165.
  - (9) Becke, A. D. *Phys. Rev.* **1988**, A38, 3098.
  - (10) (a) Perdew, J. P.; Zunger, A. *Phys. Rev.* **1981**, B23, 5048. (b) Perdew, J. P. *Phys. Rev.* **1986**, B33, 8822.

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